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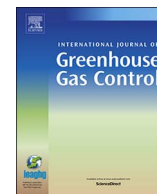
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Oxygen isotopes as a tool to quantify reservoir-scale CO₂ pore-space saturation



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ABSTRACT

Structural and residual trapping of carbon dioxide (CO₂) are two key mechanisms of secure CO₂ storage, an essential component of Carbon Capture and Storage technology. Estimating the amount of CO₂ that is trapped by these two mechanisms is a vital requirement for accurately assessing the secure CO₂ storage capacity of a formation, but remains a key challenge. Here, we review recent field and laboratory experiment studies and show that simple and relatively inexpensive measurements of oxygen isotope ratios in both the injected CO₂ and produced water can provide an assessment of the amount of CO₂ that is stored by residual and structural trapping mechanisms. We find that oxygen isotope assessments provide results that are comparable to those obtained by geophysical techniques. For the first time we assess the advantages and potential limitations of using oxygen isotopes to quantify CO₂ pore-space saturation based on a comprehensive review of oxygen isotope measurements from reservoir waters and various global CO₂ injection test sites. We further summarise the oxygen isotope composition of captured CO₂ in order to establish the controls on this fingerprint.

1. Introduction

Carbon Capture and Storage and/or Utilisation (CCS or CCU) involves capturing and purifying carbon dioxide (CO₂), compressing, transporting and injecting it into the geological subsurface, particularly deep saline aquifers, depleted hydrocarbon fields, basalt formations or coal seams. Capture and subsequent geological storage of CO₂ in rock formations is a commercially available means of reducing CO₂ emissions to the atmosphere from fossil fuel combustion for power generation and industrial processes. When combined with the combustion of biomass (BECCS) the technology provides the only currently available large-scale negative emissions technology (Scott et al., 2013). Recent CO₂ storage estimates provide confidence that there is global capacity to store significant quantities of CO₂ (Hitchon, 1996; Holloway, 1997; Metz et al., 2005). After injection commences, CO₂ is initially stored in sedimentary formations via three different mechanisms: (1) structural and stratigraphic trapping, where CO₂ is trapped beneath an impermeable cap rock, (2) residual trapping, the immobilisation of CO₂ through trapping within individual and dead end spaces between rock grains, and (3) solubility trapping, where CO₂ is dissolved into the

reservoir water that fills the pores between rock grains. Studies of natural CO₂ reservoirs and CO₂ test injection sites have shown that structural and stratigraphic trapping and residual trapping are almost instantaneous trapping mechanisms, with dissolution trapping requiring more time for the CO₂ to dissolve which varies depending on the amount of CO₂ injected relative to available water and often proximity to an actively recharging aquifer (Scott et al., 2013). Mineral trapping of CO₂ as a result of chemical reactions between the injected CO₂ and the host rock to form new carbonate minerals within the pores is a longer term storage mechanism in sedimentary formations. Depending on the mineralogy of the reservoir rocks, mineral trapping may play a role after a few decades to several hundreds of years after initiation of CO₂ injection (e.g., Audigane et al., 2007; Sterpenich et al., 2009; Xu et al., 2004), though a number of natural CO₂ reservoirs do not show evidence for such trapping (Gilfillan et al., 2008, 2009). Mineral trapping of injected CO₂ can occur more quickly in reactive basaltic rocks and where CO₂ is pre-mixed with water as shown by recent experiments undertaken in Iceland (Matter et al., 2016) and northwest USA (McGrail et al., 2017).

In order to accurately model the long-term fate of CO₂ in the

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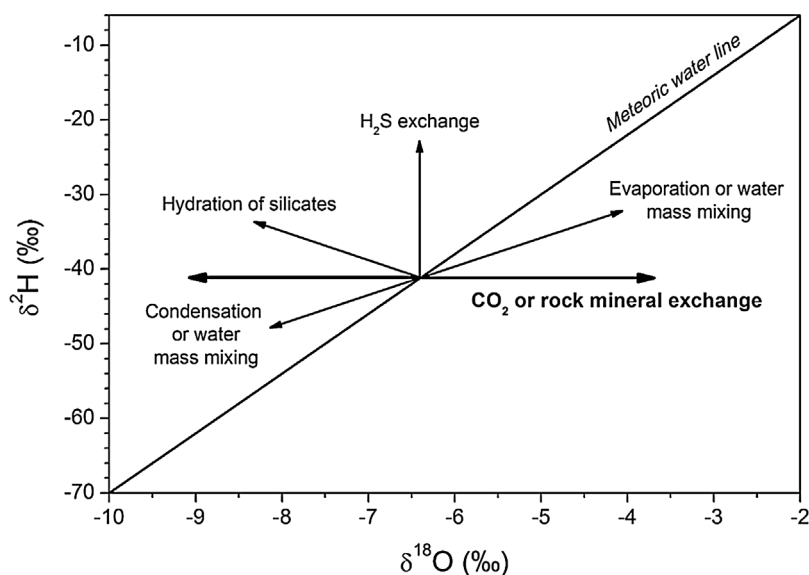


Fig. 1. Processes that can modify the stable oxygen and hydrogen isotope composition of reservoir water (modified from D'Amore and Panichi, 1985). Note that formation waters tend to lie between the meteoric water line (Craig, 1961) and the line defining CO₂ or mineral exchange.

injection formation of a commercial-scale CCS project, it is helpful to quantitatively assess the amount of structural, residual and solubility trapping acting on the reservoir scale. Whilst laboratory core flood experiments on samples taken from the injection formation can provide some indication of the degree of CO₂ trapping expected (e.g., Krevor et al., 2012, 2015), these are limited to the individual sample and up-scaling the results to the entire reservoir is notoriously difficult. A reservoir-scale short-term test undertaken at the field site prior to large-scale injection can help to reduce the risk and uncertainty in estimating the CO₂ storage capacity of a formation and provides a commercial operator with greater reassurance of the viability of their proposed storage site. This is particularly true for two of the CO₂ storage mechanisms, structural and residual trapping of CO₂, which we combine here with the term “CO₂ pore-space saturation”. These two mechanisms can play a major role for CO₂ plume migration, immobilisation, storage security and reservoir management (Doughty and Pruess, 2004; Ennis-King and Paterson, 2002; Juanes et al., 2006; Krevor et al., 2015; Qi et al., 2009). Despite the important role of these trapping mechanisms in commercial-scale CCS projects, there is a current lack of cost-effective and reliable methodologies to estimate their extent on the reservoir scale (Mayer et al., 2015). Geophysical approaches to determine CO₂ pore-space saturation have a number of limitations, for example thin layers are not resolvable due to seismic resolution (Wells et al., 2006), while well-based geophysical technologies such as pulsed neutron logging are restricted to the region of pore space in the vicinity of the well (~25 cm; Dance and Paterson, 2016).

Stable oxygen isotopes of water and CO₂ may be highly suitable for assessing CO₂ pore-space saturation (Mayer et al., 2015). As inherent tracers, stable isotopes are relatively inexpensive, particularly when compared to other artificial or added geochemical tracers like noble gases, perfluorocarbon tracers or sulfur hexafluoride. Studies from several CO₂ storage sites in Canada (Johnson et al., 2011), the USA (Kharaka et al., 2006) and Australia (Serno et al., 2016), along with laboratory experiments (Barth et al., 2015; Johnson and Mayer, 2011), have shown that the oxygen isotope ratio (δ¹⁸O) of reservoir water can change, without a change in the hydrogen isotope composition of the water, due to isotopic equilibrium exchange between the reservoir water and CO₂ added to the reservoir. These studies revealed that the change in the δ¹⁸O value of the reservoir water due to oxygen isotope exchange with CO₂ under conditions typical for CO₂ injection sites can be related to the fraction of oxygen in the system sourced from CO₂ (Barth et al., 2015; Johnson and Mayer, 2011; Johnson et al., 2011; Kharaka et al., 2006; Serno et al., 2016). Several studies have consequently provided evidence that this change can be successfully used to assess volumetric saturation of free-phase CO₂ in the reservoir (Johnson

et al., 2011; Li and Pang, 2015; Serno et al., 2016).

In order to improve the application of oxygen isotopes to quantitatively assess CO₂ pore-space saturations on a reservoir scale in future CO₂ storage projects, we present a review of findings from several CO₂ injection field experiments around the globe using oxygen isotope ratios to quantify CO₂ pore-space saturation. Furthermore, we summarise published δ¹⁸O values from captured CO₂ as a potential CO₂ source for field injection tests and make hypothetical predictions regarding the expected δ¹⁸O values of captured CO₂ where current data are unavailable or incomplete.

2. Geochemical background

2.1. Changes in the oxygen isotope ratios of reservoir water

Stable isotope analyses of water commonly measure ²H/¹H, as δ²H, and ¹⁸O/¹⁶O, as δ¹⁸O, where δ represents the isotope ratio in ‰ relative to Vienna Standard Mean Oceanic Water (VSMOW):

$$\delta_{\text{sample}} = \left(\frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1 \right) \times 1000 \quad (1)$$

R represents the ¹⁸O/¹⁶O or ²H/¹H ratio of samples and the VSMOW standard. All stable isotope ratios in this manuscript are reported in ‰ relative to VSMOW.

For meteoric water, the source of most waters in sedimentary formations, δ²H and δ¹⁸O co-vary with values falling along the meteoric water line (Fig. 1). Changes to this trend result from isotope fractionation (e.g. during evaporation) or addition of other hydrogen and/or oxygen sources with different isotope compositions. Significant sources of oxygen in geological reservoirs, other than the reservoir water, are native CO₂ derived from geological processes, dissolved inorganic carbon, oxygen within the molecular structure of hydrocarbons, and oxygen in mineral grains (silicates and carbonates) of the host rock formation (Johnson et al., 2011; Mayer et al., 2015).

The sources of reservoir oxygen are typically in isotopic equilibrium with the reservoir fluid due to fast reaction kinetics of the oxygen isotope system (e.g., Karolytė et al., 2017; Mills and Urey, 1940; Raistrick et al., 2009; Vogel et al., 1970). In most natural environments, the amount of oxygen in reservoir CO₂ is negligible compared to that in water, resulting in the reservoir water δ¹⁸O values remaining essentially constant and the δ¹⁸O value of CO₂ (δ¹⁸O_{CO₂}) approaching that of the water plus the appropriate isotopic enrichment factor between water and CO₂ ($\epsilon_{\text{CO}_2-\text{H}_2\text{O}} \approx 10^3 \ln \alpha_{\text{CO}_2-\text{H}_2\text{O}}$) at the reservoir temperature (Bottinga, 1968). $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$ is reported in ‰ and determined using Eq.

(2), defined by Bottinga (1968) and discussed in Friedman and O'Neil (1977):

$$\epsilon_{\text{CO}_2-\text{H}_2\text{O}} = -0.0206 \times \left(\frac{10^6}{T^2} \right) + 17.9942 \times \left(\frac{10^3}{T} \right) - 19.97 \quad (2)$$

where T is the reservoir temperature in Kelvin. This equation is valid at atmospheric conditions as well as elevated temperatures and pressures relevant for CCS projects (Becker et al., 2015; Bottinga, 1968; Johnson et al., 2011). $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$ typically varies between 26 and 40‰ (for reservoir temperatures of 25–120 °C).

Oxygen isotope exchange proceeds readily between CO_2 and water, and so injection of large amounts of CO_2 into the reservoir will result in an oxygen isotope shift away from formation water baseline values, while $\delta^2\text{H}$ values remain constant (e.g., Clark and Fritz, 1997; Craig, 1963; D'Amore and Panichi, 1985; Johnson and Mayer, 2011; Johnson et al., 2011; Lions et al., 2014). Kampman et al. (2014) suggested that diffusive oxygen isotope exchange on a small scale takes place in minutes so that CO_2 and water should be in equilibrium in the pore space. At larger spatial scales, the rate of oxygen isotope exchange varies with salinity and temperature. Lécuyer et al. (2009) measured the time taken to attain CO_2 – H_2O isotopic equilibrium for reservoir waters of varying salinities; they found that waters with 0 g/L total dissolved solids (TDS) achieved isotopic equilibrium within 4 h, while waters with 250 g/L TDS required 12 h. Vogel et al. (1970) established that oxygen isotope equilibrium between CO_2 and demineralised water was established within 22 h at 25 °C and faster at higher temperatures. Slightly longer timescales of 4–7 days were measured for establishment of equilibrium between supercritical CO_2 and water (Becker et al., 2015; Johnson and Mayer, 2011). In the case of CO_2 injection, oxygen isotope equilibrium is thus expected to be attained in a matter of days.

An oxygen isotope shift in reservoir water can also be produced via mineral dissolution contributing oxygen previously bound in mineral lattices to the system, especially for carbonate minerals. However, the contribution of this process to changes in $\delta^{18}\text{O}$ values of reservoir water is usually small relative to the effect caused by injected CO_2 (Johnson et al., 2011); laboratory experiments investigating limestone dissolution in CO_2 saturated water at 150 bar and 80 °C, and water-rock ratios 40 times higher than typical for storage reservoirs showed that less than 1% of the limestone mass dissolved (Sterpenich et al., 2009).

2.2. Quantifying CO_2 pore-space saturation based on oxygen isotope equilibrium exchange between reservoir water and CO_2

A quantitative method to estimate CO_2 pore-space saturation, based on changes in the $\delta^{18}\text{O}$ value of reservoir water in contact with free-phase CO_2 , was first proposed and utilised by Kharaka et al. (2006) and has been further described and applied by Johnson et al. (2011). During CO_2 injection into a storage reservoir, a new major source of oxygen is added to the system in the form of supercritical CO_2 , and the $\delta^{18}\text{O}_{\text{CO}_2}$ value will start to control the oxygen isotope composition of the water- CO_2 system. The $\delta^{18}\text{O}$ value of reservoir water will start to change from the baseline oxygen isotope value, $\delta^{18}\text{O}_{\text{H}_2\text{O}}^b$, towards an end-member scenario where the water has a final value, $\delta^{18}\text{O}_{\text{H}_2\text{O}}^f$, lower than that of the CO_2 by $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$. Consequently, both CO_2 and water $\delta^{18}\text{O}$ values will change due to isotopic equilibrium exchange reactions (Barth et al., 2015; Johnson and Mayer, 2011; Johnson et al., 2011; Kharaka et al., 2006; Mayer et al., 2015; Serno et al., 2016). The fraction of oxygen in the system sourced from CO_2 , $X_{\text{CO}_2}^o$, can be estimated using Eq. (3):

$$X_{\text{CO}_2}^o = \frac{(\delta^{18}\text{O}_{\text{H}_2\text{O}}^b - \delta^{18}\text{O}_{\text{H}_2\text{O}}^f)}{(\delta^{18}\text{O}_{\text{H}_2\text{O}}^b + \epsilon_{\text{CO}_2-\text{H}_2\text{O}} - \delta^{18}\text{O}_{\text{CO}_2})} \quad (3)$$

A subsequent oxygen isotope change of the reservoir water due to injected CO_2 requires that the difference in $\delta^{18}\text{O}$ values between the CO_2 and water is different to the isotopic enrichment factor $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$. If other significant oxygen sources that may promote oxygen isotope

shifts of reservoir water can be ruled out, then any shift in the $\delta^{18}\text{O}$ value of reservoir water indicates that the water must be in contact with the injected CO_2 . The magnitude of the shift in $\delta^{18}\text{O}_{\text{H}_2\text{O}}^f$ can be used to assess the relative contributions from dissolved and free-phase CO_2 . If reservoir conditions and $\delta^{18}\text{O}_{\text{CO}_2}$ are known, CO_2 solubility can be calculated (Duan and Sun, 2003), along with a theoretical $\delta^{18}\text{O}$ value of fully CO_2 -saturated reservoir water. When the $\delta^{18}\text{O}$ value of reservoir water changes by less than is predicted for maximum CO_2 dissolution, then the water is under-saturated and any free-phase CO_2 in contact with this water will continue to dissolve (Johnson et al., 2011). A larger $\delta^{18}\text{O}$ shift than predicted for maximum CO_2 dissolution means that the water is over-saturated with CO_2 , and there is thus a free phase of CO_2 (gas, supercritical or liquid) in contact with the water providing excess oxygen to the system. In these circumstances, free-phase (i.e. structurally and residually trapped) CO_2 pore-space saturation (S_{CO_2}) can be estimated via Eq. (4), which quantitatively describes the oxygen isotope water- CO_2 system:

$$S_{\text{CO}_2} = \frac{(BX_{\text{CO}_2}^o + CX_{\text{CO}_2}^o - B)}{(A - B - AX_{\text{CO}_2}^o + BX_{\text{CO}_2}^o + CX_{\text{CO}_2}^o)} \quad (4)$$

with A = mol of oxygen in 1 L of free-phase CO_2 at reservoir conditions, B = mol of oxygen dissolved in 1 L water from CO_2 at reservoir conditions, C = mol of oxygen in 1 L water at reservoir conditions, and $X_{\text{CO}_2}^o$ derived from Eq. (3) (Johnson et al., 2011).

Eq. (4) was first applied during the Pembina Cardium CO_2 Monitoring Pilot in Alberta, Canada, to estimate S_{CO_2} (Johnson et al., 2011). In specific field setups when CO_2 is co-injected with water/brine, for example during the Otway Stage 2 B experiments, the method can be used to provide an estimate of residual CO_2 saturation. This method assumes a closed system and can only be applied if isotopic exchange with minerals in the reservoir, and processes such as gravitational mixing (Riaz et al., 2006) are negligible. Reservoir water may be sampled for oxygen isotope analyses at the wellhead of observation or production wells without being affected by degassing of CO_2 since the isotopic equilibrium between water and injected CO_2 is established before the CO_2 exsolves (Johnson et al., 2011). However, subsequent sample storage should assure prevention of evaporation of water so that its isotopic composition is not altered. Ideally, samples should be collected using a downhole sampling tool like the U-tube sampling system (Freifeld et al., 2005) and, if analysis is not to be completed immediately, with a complete degassing of CO_2 at surface to prevent continuous oxygen isotope equilibrium exchange between the water and the incompletely degassed CO_2 in the sampling vessel during storage.

2.3. Oxygen isotope laboratory tests assessing CO_2 pore-space saturation

Johnson and Mayer (2011) investigated different water- CO_2 systems in 150 mL stainless steel cylinders with variable CO_2 pressures up to 190 bar (and resulting CO_2 concentrations), with CO_2 contributing up to 35% of the oxygen in the cylinder. The initial $\delta^{18}\text{O}_{\text{CO}_2}$ value was +0.9‰, and waters with an artificially ^{18}O -enriched $\delta^{18}\text{O}_{\text{H}_2\text{O}}^b$ value of +235.1‰ were used in order to observe changes in the $\delta^{18}\text{O}$ values of both CO_2 and water of several tens ‰. A temperature of 50 °C was used, for which a constant water $\delta^{18}\text{O}$ of 35.5‰ lower than that of the CO_2 was expected when oxygen isotope equilibrium is maintained, and the reaction was undertaken over one week.

The experiments with variable fractions of oxygen sourced from CO_2 showed that the larger the increase in the CO_2 -sourced oxygen fraction (the larger the pressure in the reaction vessel), the larger the decrease in water $\delta^{18}\text{O}$ from its baseline value towards a value approaching that of the original CO_2 plus $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$ (Johnson and Mayer, 2011). The oxygen isotope difference between water and CO_2 remained constant at $36.4 \pm 2.2\%$ (1σ , $n = 15$), identical to the theoretical value of 35.5‰. This suggests that independent of the CO_2 concentration,

oxygen isotope equilibrium between CO₂ and water was established within the one-week experimental period. Hydrogen isotope ratios of the water remained unchanged throughout the experiments. The observed oxygen isotope shifts in the water matched calculated CO₂ fractions within uncertainties for each given X_{CO₂}⁰ value following Eq. (3). This provided evidence that CO₂ at elevated concentrations typical for CO₂ storage sites changes the water δ¹⁸O value in a predictable way. Hence, the Johnson et al. (2011) approach can be used to robustly estimate S_{CO₂} in a geological storage reservoir over a range of CO₂ pressures, including that of supercritical CO₂, provided that the oxygen isotope ratios of CO₂ and water are sufficiently distinct. Li and Pang (2015) further used the isotopic data from the laboratory experiment conducted by Johnson and Mayer (2011) for the case of 30 mL water and 120 mL CO₂ at a pressure of 186 bar and 50 °C, and Eq. (4) to estimate a S_{CO₂} value of 79%, equivalent to the actual value of 80%.

Barth et al. (2015) performed similar laboratory experiments to those of Johnson and Mayer (2011), using ambient pressures and no ¹⁸O labelling for water and CO₂. This allowed them to study the isotopic exchange between water and CO₂ at natural concentration levels, using an initial δ¹⁸O_{CO₂} of +9.3‰ and δ¹⁸O_{H₂O} of −8.7‰. In their experiments, they varied the amount of water (between 5 and 100 mL) that was exposed to CO₂ in 1 L glass flasks. The flasks were shaken for up to 222 h on an orbital shaker at room temperatures (22 °C). Their observed changes in water δ¹⁸O values were similar to theoretically predicted values based on the approach of Johnson et al. (2011), further indicating the robustness of Eqs. (3) and (4) for variable temperatures and pressures.

3. Field applications of oxygen isotope assessments of CO₂ pore-space saturation

3.1. Pembina

During the Enhanced Oil Recovery (EOR) Pembina Cardium CO₂ Monitoring Pilot in the Pembina area west of Edmonton, Alberta (Canada), two phases of CO₂ injection (total of ~75,000 t of liquid CO₂ trucked to the site and injected in supercritical state) were conducted between March 2005 and March 2008 into the Upper Cretaceous Cardium Formation, a siliciclastic reservoir with sandstones interbedded with shales (Johnson et al., 2011). The measured reservoir temperature was 50 °C and the pressure was ~190 bar at a depth of ~1650 m (Hitchon, 2009). The high purity CO₂ injected during the project was delivered by Ferus Gas Industries from three different facilities where the CO₂ was captured from waste gas streams, followed by purification, liquefaction and compression. CO₂ was injected through 2 wells, with 4 observation wells for each of the 2 injection wells (Hitchon, 2009). Two of these observation wells were shared, with an additional 2 off-pattern wells for each injection well being monitored as well. TDS in baseline formation water samples varied between 3.9 and 7.6 g/L for the 8 observation wells (Johnson et al., 2011). Casing gas and fluid samples were collected monthly at the wellheads of the 8 observations wells between February 2005 and March 2008, with baseline data collected between February and April 2005 (Johnson et al., 2011). Following the baseline sampling and start of CO₂ injection, 15 geochemical monitoring events took place between May 2005 and January 2007, followed by an EOR operation switch to a water-alternating gas (WAG) regime in February 2007, with a further 13 monitoring campaigns completed until March 2008 (Johnson et al., 2011).

The δ¹⁸O_{CO₂} value of injected CO₂ was +28.6 ± 0.2‰ (Johnson et al., 2011). The baseline δ¹⁸O values of the reservoir water at the 8 observation wells varied between −13.5 ± 0.2 and −17.1 ± 0.2‰, dependent upon the impact of a previous water-flood of the reservoir (Table 1). Following initiation of CO₂ injection, reservoir water δ¹⁸O values increased between 1.1 and 3.9‰ at 3 of the 8 observation wells prior to the start of the WAG operation (Fig. 2). This increase was

Table 1
Summary of oxygen isotope data from CCS storage projects.

Project	Location	Reservoir Geology	Total injected CO ₂ (tonnes)	CO ₂ source	δ ¹⁸ CO ₂ (‰ VSMOW)	Baseline δ ¹⁸ O _{H₂O} (‰ VSMOW)	Change in δ ¹⁸ O _{H₂O} (‰ VSMOW)	Time for change	References
Pembina Frio-1	Alberta (Canada) East Texas (USA)	Cretaceous arenite; EOR Oligocene sandstone; saline aquifer	75,000 1600	Natural gas processing Refinery; fertiliser plant	+28.6 ± 0.2 + 9	−17.1 to −13.5 + 0.8	1.1–3.9 11.9	22 months 6 months	Johnson et al. (2011) Hovorka et al., (2006), Kharaka et al. (2006, 2009) Serno et al. (2016)
Otway 2Bext	Southwest Victoria (Australia)	Cretaceous sandstone; saline aquifer	109.8	Pure CO ₂ production; oxyfuel combustion	+28.94 ± 0.12	−6.3 to −5.6	0.26	up to 2 days	Serno et al. (2016)
Ketzin	Brandenburg (Germany)	Triassic greywacke; saline aquifer	67,271	Hydrogen production in oil refinery; oxyfuel combustion	−19.2 ± 14.5	−5.6 to −5.2	1.9	6 months	Martens et al. (2012), Myrtilinen et al. (2010), Nowak et al. (2014)
IEA GHG Weyburn-Midale	Saskatchewan (Canada)	Mississippian carbonate; depleted oil field/EOR	5,000 per day	Coal gasification	+3.8 ± 0.2	−9.82 to −1.22	2.4–9.3	minimum 3 years, mostly > 8 years	Emberley et al. (2005), Johnson et al. (2009), this study

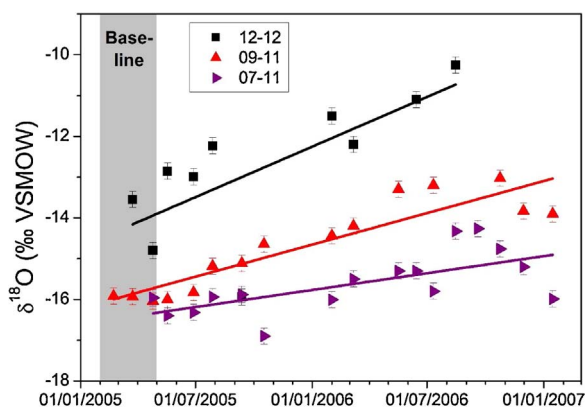


Fig. 2. Oxygen isotope composition of reservoir waters collected from the 3 wells (12–12 in black, 09–11 in red, 07–11 in purple) during the EOR Pembina Cardium CO₂ Monitoring Pilot that showed an isotopic shift from baseline values (Johnson et al., 2011). All samples shown here were collected prior to WAG injection. The grey bar indicates the baseline monitoring period. Linear fits to the data are shown as solid lines. Errors for $\delta^{18}\text{O}$ are reported analytical uncertainties ($\leq \pm 0.2\text{‰}$; Johnson et al., 2011). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

accompanied by breakthrough of CO₂ at these 3 wells, and hence the shifts in $\delta^{18}\text{O}$ values of the reservoir water were interpreted to be due to oxygen isotope equilibrium exchange between the injected CO₂ and water.

Consequently, the mass of injected CO₂ was large enough to influence the oxygen isotope composition of the reservoir water during the Pembina Pilot, and the Johnson et al. (2011) approach presented in Section 2.2 was first used here to estimate CO₂ pore-space saturations. Full saturation of the reservoir water with CO₂ would only have resulted in an increase of a maximum of 0.4‰ in the $\delta^{18}\text{O}$ values of reservoir water. Similarly, contributions of oxygen from mineral dissolution have been found to represent less than 0.01% of total oxygen. Johnson et al. (2011) therefore used the oxygen isotope data to quantify CO₂ pore-space saturation using Eq. (4), resulting in S_{CO_2} estimates ranging between 12 and 64% for the vicinity of the 3 different observation wells with the largest $\delta^{18}\text{O}$ changes in reservoir water. Unfortunately, no data from alternative techniques that could provide comparative CO₂ pore-space saturations were published for the Pembina Pilot.

Immediately following the start of the WAG operation in February 2007, reservoir water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values showed variable responses for the different observation wells, with increasing, constant or decreasing isotopic values as opposed to values prior to the switch to the WAG regime (Johnson et al., 2011). The differences in oxygen and hydrogen isotope behaviour between the different wells may be due to a variable influence of the injected water isotopic signature on the existing reservoir water isotope regime. In this case, oxygen isotopes may not be suited to quantify CO₂ pore-space saturation during WAG operation at an EOR field site.

3.2. Frio

During the Frio-1 experiment at the Frio site located within the South Liberty oil field in east Texas (USA), 1600 t of CO₂ were injected during 4–14th October 2004 at 1528–1534 m depth into a 24-m-thick high-permeability sandstone unit of the Oligocene Frio Formation (Hovorka et al., 2006; Kharaka et al., 2006, 2009). The reservoir is characterised by a Na-Ca-Cl type formation water with 93 g/L TDS, and reservoir temperatures and pressures of 60 °C and 150 bar, respectively (Hovorka et al., 2006). As the Frio Formation has a dip of 16° to the south, an observation well was used 30 m up-dip of the injection well to monitor the target interval. The injected CO₂ was refrigerated liquid

CO₂ trucked to the site, and sourced from a Bay City refinery in Texas and a Donaldsonville fertiliser plant in Louisiana. The injected CO₂ for the Frio-1 experiment had a reported oxygen isotope value of +9‰ (Kharaka et al., 2006), with no further information about the $\delta^{18}\text{O}$ values of the CO₂ produced by each of the two sources or their mixing proportions.

CO₂ and water samples collected during the Frio-1 experiment using a U-tube system and Kuster downhole sampler (baseline and post-injection geochemical sampling) have provided evidence that the $\delta^{18}\text{O}$ value of the reservoir water changed due to interaction with free-phase CO₂ (Kharaka et al., 2006) (Table 1). The $\delta^{18}\text{O}$ values of the reservoir water shifted from a baseline value of +0.8‰ to a minimum of −11.1‰, with a corresponding increase in the CO₂ oxygen isotope composition from +9‰ to up to +43‰. Kharaka et al. (2006) used the oxygen isotope compositions from the reservoir water and CO₂ in mass balance equations to estimate the water to CO₂ mass and volume ratios in the reservoir. The oxygen isotope compositions of the water and CO₂ from the observation well indicated that initially the system was brine dominated. CO₂ pore-space saturation was calculated to be $\sim 10 \pm 3\%$ over the 30 days following CO₂ breakthrough at the observation well (Kharaka et al., 2006). Samples collected from the injection well on 4–6th April 2005 yielding the maximum oxygen isotope shift indicated that CO₂ filled $\sim 50\%$ of the pore-fluid volume 6 months after the end of injection. Johnson et al. (2011) used their technique and estimated S_{CO_2} values for the Frio-1 experiment for the same time periods, with results of 8% for the first day after CO₂ breakthrough and 59% for early April 2005. Consequently, their results are very similar to those of the Kharaka et al. (2006) non-equilibrium oxygen isotope approach.

Downhole pulsed neutron logging showed average CO₂ pore-space saturations of $\sim 18.5\%$ on day 4 and $\sim 34\%$ on day 10 (Hovorka et al., 2006). Results from pulsed neutron logging after 6 months indicated that the near-wellbore CO₂ pore-space saturation increased to $\sim 50\%$, very similar to the oxygen isotope-based S_{CO_2} estimate (Hovorka et al., 2006). Saturations from arrival times of CO₂ and injected tracers (perfluorocarbon tracers, krypton, xenon and sulfur hexafluoride) and using mass balances in a simple radial flow model ranged between 15.6 and 17.1% over the few days following CO₂ breakthrough (Freifeld et al., 2005). No tracer method results were reported after the first month following the CO₂ injection. Kampman et al. (2014) suggested that due to the dip of the reservoir, the radial flow model probably over-estimates the volume occupied by CO₂ and therefore under-estimates the calculated CO₂ pore-space saturations. It therefore remains problematic to directly compare the model- and oxygen isotope-based S_{CO_2} estimates. Despite these issues, the comparison of the results based on oxygen isotope data and pulsed neutron logging, for the time period immediately following CO₂ breakthrough at the observation well ($10 \pm 3\%$ from oxygen isotopes and 18.5% from pulsed neutron logging) and 6 months later ($\sim 50\%$ for both the geochemical and geophysical methods), provides evidence that the oxygen isotope approach can be used as a tool to quantify CO₂ pore-space saturation.

3.3. Otway

Serno et al. (2016) used oxygen isotope data from samples obtained during the recent CO2CRC Otway Stage 2 B Extension (hereafter referred to as “Otway 2Bext”) conducted in October–December 2014 over a time span of 80 days at the CO2CRC Otway Facility in the Otway Basin in southwest Victoria (Australia) to estimate the levels of residual CO₂ trapping. The single-well configuration of Otway 2Bext allows fluids to be injected and back-produced through the same well, as opposed to inter-well tests in which fluids are injected in one well and produced through another nearby production or observation well.

During Phase 2 of the field test, 109.8 t of CO₂ sourced from the nearby Boggy Creek production well (99.9% purity) and from the Callide A Oxyfuel Project capture plant in central Queensland were injected at 1392–1399 m true vertical depth subsea (TVDSS) into the

Paaratte Formation (Serno et al., 2016), a complex Upper Cretaceous interbedded formation of medium to high permeability sandstones and thin carbonaceous mud-rich lithologies (Bunch et al., 2012; Dance et al., 2012; Paterson et al., 2013). TDS of the reservoir fluid was 0.8 g/L (Bunch et al., 2012; Dance et al., 2012). The well was equipped with downhole temperature and pressure sensors, which continuously monitored near-well reservoir conditions in the target interval.

The field experiments consisted of a first phase to study differences in reservoir water quality in response to the injection of CO₂-saturated water with and without trace amounts of gas impurities (Haese et al., 2016). Phase 2 was a field test to characterise the residual trapping levels of CO₂ (LaForce et al., 2015; Serno et al., 2016), and was conducted in four different stages:

- Phase 2.1: Injection and production of reservoir water without CO₂ (water test)
- Phase 2.2: Pure CO₂ injection over a period of 4 days
- Phase 2.3: Injection of fully CO₂-saturated water to drive the reservoir to residual saturation
- Phase 2.4: Injection and production of fully CO₂-saturated water (residual saturation test)

Reservoir CO₂ and water samples were collected throughout Phases 1 and 2 using a U-tube system installed in the well (Freifeld et al., 2005). Prior to the drive to residual saturation, baseline $\delta^{18}\text{O}$ values of the reservoir water remained constant within a 1σ uncertainty for all sampled baseline samples with a range between ~ -6.3 and -5.6‰ (Serno et al., 2016) (Table 1). Following the initiation of the drive to residual saturation in the reservoir, the water $\delta^{18}\text{O}$ values decreased from a baseline value of the fully CO₂-saturated water back-produced from the reservoir, $-5.9 \pm 0.1\text{‰}$, to $-6.1 \pm 0.1\text{‰}$ within a maximum of 2 days (Fig. 3). Any contribution of oxygen from mineral dissolution was excluded (Serno et al., 2016).

The first 12.2 t of the injected CO₂ that was residually trapped in the reservoir were Callide CO₂ with a $\delta^{18}\text{O}_{\text{CO}_2}$ value of $+26.1 \pm 0.1\text{‰}$, while the remaining 97.6 t was Boggy Creek CO₂ with a $\delta^{18}\text{O}_{\text{CO}_2}$ value of $+29.3 \pm 0.2\text{‰}$. Since no estimates for the mixing of the CO₂ in the reservoir or of variable oxygen isotope signatures of the CO₂ in contact with water in the reservoir were available, Serno et al. (2016) assumed perfect mixing of these two CO₂ sources in the reservoir and derived an average $\delta^{18}\text{O}_{\text{CO}_2}$ value of $+28.9 \pm 0.1\text{‰}$ based on the amounts of the

two injected CO₂ sources. Considering the reservoir water baseline and injected CO₂ $\delta^{18}\text{O}$ values, and the reservoir conditions during the field experiment (reservoir pressure varied between 139.3 and 139.5 bar during Phase 2.4, and reservoir temperature between 42.5 and 47.0 °C, with an average $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$ value of 36.8‰), a change to up to 2‰ lower $\delta^{18}\text{O}$ values of the reservoir water was expected when CO₂-water oxygen isotope equilibrium exchange occurs in the reservoir.

The data from this study were the first to indicate that a change in reservoir water $\delta^{18}\text{O}$ values ($-0.3 \pm 0.2\text{‰}$) due to oxygen isotope equilibrium exchange between the trapped CO₂ and water occurs over a time span of only a few days. As a result of the field experiment setup, with no structurally trapped CO₂ in the reservoir, Serno et al. (2016) used Eq. (4) to estimate a residual CO₂ saturation of $14 \pm 9\%$ for this sample. Although the oxygen isotope shift observed in the reservoir water during Otway 2Bext was relatively small, the oxygen isotope-based result compares well with independent measures from pulsed neutron logging (averaged near-well reservoir saturation of $\sim 8.8\%$) and of numerical simulation of Kr and Xe tracer injection and recovery data during the field experiment (best estimates between 7.2 and 9.3%) (LaForce et al., 2015), indicating the potential of oxygen isotopes to serve as a geochemical tool to quantify reservoir CO₂ saturation over a time span of only a few days in a single-well configuration test. Furthermore, the choice of a more isotopically distinct injected CO₂ has the potential to improve the accuracy of the isotope-based assessment of residual CO₂ saturation in such field experiments.

3.4. Ketzin

During the CO₂SINK project (“CO₂ Storage by Injection into a Natural Saline Aquifer at Ketzin” – subsequently referred to as the “Ketzin project”) at the Ketzin test site near Berlin (Germany), a total of 67,271 t of CO₂ was injected at a depth of ~ 650 m from 30th June 2008 for 62 months (Martens et al., 2012). CO₂ was injected into the 80 m thick and lithologically heterogeneous Upper Triassic Stuttgart Formation consisting of sandstones and siltstones interbedded with mudstones (Förster et al., 2006). One injection well (Ktzi 201) and 2 observation wells (Ktzi 200 and 202) were used during the field experiment, with Ktzi 201 and 202 being situated 50 and 100 m apart from Ktzi 200, respectively (Myrntinen et al., 2010). Reservoir temperatures and pressures at 650 m depth were ~ 35 °C and 62 bar, respectively, with a reservoir water TDS of 235 g/L (Myrntinen et al.,

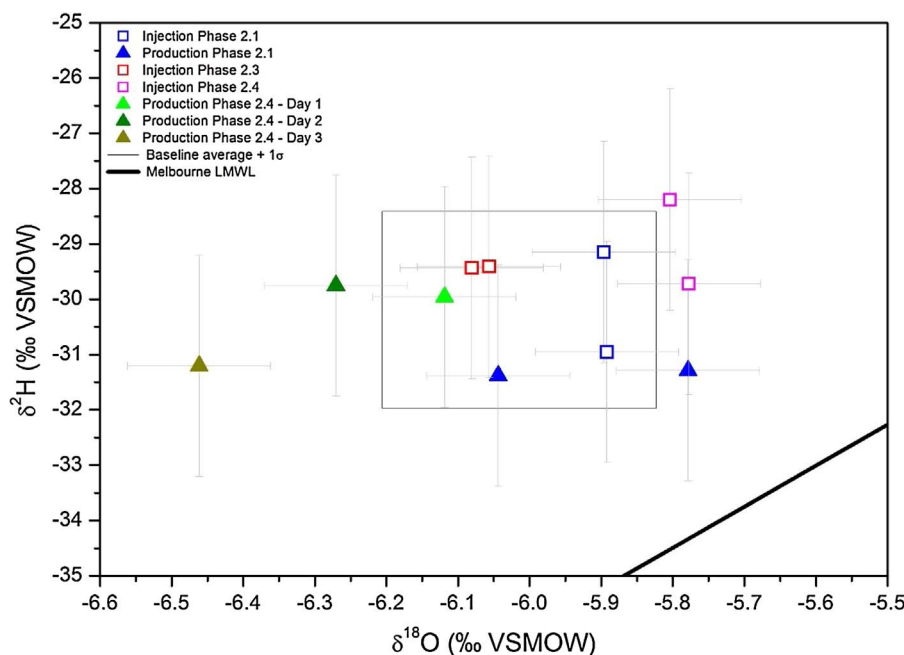


Fig. 3. $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ values in water samples from Phases 2.1, 2.3 and 2.4 of Otway 2Bext (Serno et al., 2016). Samples from injection and production periods are shown as open and filled symbols, respectively. U-tube samples are shown as triangles, and bottle samples collected from the production line at surface as squares. Samples from Phase 2.1 are in blue, from Phase 2.3 in red, from the water injection for Phase 2.4 in magenta, and from the water production of Phase 2.4 in different green colours. The thick black line indicates the Local Meteoric Water Line (LMWL) for Melbourne (Hughes and Crawford, 2012), and the black box symbolises the 1σ range of the baseline water samples prior to water production for Phase 2.4. Injection water from Phases 2.3 and 2.4 provide the reservoir water baseline $\delta^{18}\text{O}$ range for the samples produced during Phase 2.4 (Serno et al., 2016). Error bars represent the analytical uncertainty for $\delta^{18}\text{O}$ ($\pm 0.1\text{‰}$) and $\delta^2\text{H}$ ($\pm 2.0\text{‰}$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2010; Schilling et al., 2009). The injected CO₂ originated from two sources; the primary source was Linde AG food grade CO₂ (99.9% purity) that was a by-product of hydrogen production (Martens et al., 2012). Up to the end of September 2011, a total of 51,500 t of the food grade CO₂ was injected. The other source was a captured CO₂ (99.7% purity) from the oxyfuel pilot plant “Schwarze Pumpe” operated by Vattenfall, of which 1515 t were injected during a trial period from 4th May to 13th June 2011 (Martens et al., 2012).

The injected food grade CO₂ had $\delta^{18}\text{O}_{\text{CO}_2}$ values ranging between -29.3 and -8.7‰ , measured between 30th April and 17th July 2009 (Myrntinen et al., 2010; Nowak et al., 2014), with a mean value of -19.2 ± 14.5 (2 σ) ‰ (Table 1). Baseline $\delta^{18}\text{O}$ values of the reservoir water at the injection and observation wells at sampling depths ranging from 625 to 760 m varied between -5.6 and -5.2‰ in June 2008 (Myrntinen et al., 2010). All reported water $\delta^{18}\text{O}$ values have a 1 σ uncertainty of $\pm 0.15\text{‰}$. Following the start of CO₂ injection, the $\delta^{18}\text{O}$ values of reservoir water at observation well Ktzi 200 remained constant between July 2008 and March 2009 at -5.5 to -5.3‰ , except for a sudden drop to -12‰ in December 2008. Similarly, the water $\delta^{18}\text{O}$ values remained constant at -5.5 to -5.3‰ between August 2008 and March 2009 at observation well Ktzi 202. Although only one reservoir water $\delta^{18}\text{O}$ value was measured from a depth of 670 m at Ktzi 201 following the start of injection, the sample from December 2008 showed a much lower value of -9.5‰ . Myrntinen et al. (2010) suggested that there is a lack of change in the oxygen isotope composition of reservoir waters during the Ketzin project, based on the lack of variability of $\delta^{18}\text{O}$ values at both observation wells. The lack of significant oxygen isotope shifts in the reservoir water at the observation wells has been interpreted to be due to the mass of injected CO₂ being too small to observe a significant shift of oxygen isotope ratios in reservoir waters. Considering the volume of injected CO₂, compared to field tests performed at Pembina, Frio or Otway, and since the baseline water and injected CO₂ oxygen isotope compositions are distinct enough to change the water oxygen isotope composition at the observation wells as a result of CO₂-water interaction considering the oxygen isotope enrichment factor $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$ of 38.2‰ for a reservoir temperature of 35 °C (Bottinga, 1968), we would expect a change in the reservoir water oxygen isotope composition at the observation wells to lower $\delta^{18}\text{O}$ values. The lack of water oxygen isotope change at the observation wells may be due to secure storage of large volumes of injected CO₂ in pore spaces and through dissolution into reservoir water between the injection and observation wells.

Although only one reservoir water $\delta^{18}\text{O}$ value was analysed from Ktzi 201 following the start of injection, it is worth comparing the resulting S_{CO_2} estimate from the oxygen isotope shift in this reservoir water sample to independent CO₂ pore-space saturation measures. The $\delta^{18}\text{O}$ value of mean baseline water at Ktzi 201 prior to CO₂ injection was -5.6 ± 0.2 (2 σ) ‰. Considering the injected $\delta^{18}\text{O}_{\text{CO}_2}$ value of -19.2 ± 14.5 (2 σ), fully CO₂-saturated reservoir water would have a $\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{b}}$ value of $-7.6 \pm 0.6\text{‰}$. With a reported $\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{f}}$ value of $-9.5 \pm 0.2\text{‰}$ and an oxygen isotope enrichment factor $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$ of 38.2‰, the fraction of oxygen sourced from CO₂ in the reservoir can be estimated as $3.8 \pm 1.6\%$. Considering the reservoir conditions mentioned above and using Eq. (4), the resulting estimate for S_{CO_2} is $12.8 \pm 9.7\%$. The large error of the calculated S_{CO_2} is mainly due to the large variability in reported $\delta^{18}\text{O}_{\text{CO}_2}$ values for the injected CO₂.

Pulsed neutron logs at Ktzi 201 were run prior to the start of CO₂ injection, and again in July 2008 shortly after CO₂ breakthrough at Ktzi 200, in June 2009 and in March 2010 (Ivanova et al., 2012). Volumetric CO₂ contents based on averaging three pulsed neutron log repeats following initiation of CO₂ injection at Ktzi 201 varied between 14 and 19% in the upper part of the target interval (634–642 m depth) and 0–3% in the bottom part (662–664 m depth), with average minimum and maximum values for the interval between 634 and 664 m of 5.5 and 10.0%, respectively (Ivanova et al., 2012). Consequently, our oxygen isotope-based S_{CO_2} value of $12.8 \pm 9.7\%$ falls within the range

of possible CO₂ saturations based on pulsed neutron logging. However, for the Ketzin project, the large range in $\delta^{18}\text{O}_{\text{CO}_2}$ values of injected CO₂ results in large S_{CO_2} uncertainties using the Johnson et al. (2011) approach, limiting its usefulness here.

3.5. Weyburn-Midale

The IEA GHG Weyburn-Midale CO₂ Monitoring and Storage project, conducted near the towns of Weyburn and Midale in southern Saskatchewan (Canada), started injecting CO₂ into the shallow marine carbonates in the Midale Beds of the Mississippian Charles Formation at ~ 1500 m depth in September 2000, and will continue injection until approximately 2033 at a rate of ~ 5000 t/day. The project combines CO₂ storage with EOR by injecting CO₂ and brine into a depleted oil field (Emberley et al., 2005). From the beginning of the CO₂ injection, the injection pattern has been dominated by simultaneous injection of CO₂ and water, or WAG injection (Hirsche et al., 2004). Reservoir pressures and temperatures are variable, but average at around 170 bar and 60 °C (Hutcheon et al., 2016). During the project, oxygen isotope data of the injected CO₂ and reservoir fluids from observation wells were collected (Johnson et al., 2009; Mayer et al., 2013).

Seventeen fluid and gas sampling surveys were conducted from August 2000 until October 2010, including a baseline sampling survey one month before the start of CO₂ injection (Mayer et al., 2013). Approximately 40–55 wells were sampled during each sampling survey, although samples were not always collected from the same wells due to periodic well servicing and production-related shutdowns. Fluid and gas samples were obtained at the wellheads, and $\delta^{18}\text{O}$ values in CO₂ and water and $\delta^2\text{H}$ values in reservoir water were determined as described in Mayer et al. (2013). Analytical uncertainties for gas and water $\delta^{18}\text{O}$ values are $< \pm 0.2\text{‰}$, with an uncertainty of $< \pm 2.0\text{‰}$ for water $\delta^2\text{H}$ values (Mayer et al., 2013). While some of the $\delta^{18}\text{O}$ data from reservoir waters collected at Weyburn-Midale wells have been presented in Johnson et al. (2009), the majority of the $\delta^{18}\text{O}$ values for formation waters and all $\delta^{18}\text{O}$ values for CO₂ and $\delta^2\text{H}$ values for formation waters from the Weyburn-Midale project are published here for the first time. Baseline $\delta^{18}\text{O}$ values of reservoir water collected from the wells varied between -9.8 and -1.2‰ , with an average of -6.6 ± 1.8 (1 σ) ‰ (Table 1). The injected CO₂ was captured after coal gasification in the Dakota Gasification Company's synthetic plant in Beulah, North Dakota, liquefied by compression and then piped to the Weyburn-Midale oil field (Emberley et al., 2005). The CO₂ gas was the first man-made source of CO₂ being used for EOR (Kharaqa et al., 2013), and had an essentially constant $\delta^{18}\text{O}_{\text{CO}_2}$ value of $+3.8 \pm 0.2\text{‰}$.

Although most of the ~ 40 monitored wells do not indicate an oxygen isotope shift from baseline conditions, repeatedly obtained samples from 5 Weyburn-Midale wells (01–11, 02–12, 05–36, b09–18, d11–12 east) displayed a clear shift to lower oxygen isotope values of reservoir water compared to the respective CO₂-saturated reservoir water baseline values (Table 2; Fig. 4). The oxygen isotope shifts of produced water obtained from the different wells are highly variable, with a maximum shift of 9.3‰ in ~ 8 years at well 01–11 and a minimum shift of 2.4‰ over 8.5 years at well 05–36. Well b09–18 showed an oxygen isotope shift of 8.3‰ from the CO₂-saturated baseline value in only 3 years following the start of CO₂ injection. The calculated S_{CO_2} values in the vicinity of the sampled wells varied between 5.4 and 35.1% (Table 2). These values can be compared to approximations of mean CO₂ saturations in the Midale Marly Formation based on time-lapse seismic imaging for four of the monitoring years (Fig. 19 in White, 2013). The approximate values for the locations of the wells indicate rather weak correlations with the oxygen isotope-based CO₂ pore-space saturations (Table 2). However, the seismic-based values are only approximated from the maps in Fig. 19 of White (2013), and therefore may be different to the actual value by more than 10%.

Finally, when interpreting changes in CO₂ pore-space saturation from the wells in the Weyburn-Midale field, we have to consider that

Table 2

Calculated CO₂ pore-space saturation based on baseline and lowest final reservoir water oxygen isotope compositions from the IEA GHG Weyburn-Midale CO₂ Monitoring and Storage project (Johnson et al., 2009; this study), using Eqs. (2)–(4). The estimated S_{CO₂} values based on oxygen isotopes are compared to approximated mean CO₂ saturations based on time-lapse seismic imaging of the Midale Marly Formation over time (Fig. 19 in White, 2013).

Well	Non-saturated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰ VSMOW)	Fully CO ₂ -saturated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰ VSMOW)	$\delta^{18}\text{O}_{\text{H}_2\text{O}}^f$ (‰ VSMOW)	Date of final water sampling	$\delta^{18}\text{O}_{\text{CO}_2}$ (‰ VSMOW)	X _{CO₂} [Eq. (3)] ^a	S _{CO₂} [Eq. (4)] ^b	S _{CO₂} (Seismic imaging – Midale Marly)	Date of seismic- based saturation estimate
01–11	–5.8	–6.8	–16.1	28–29 October 2008	+3.8 ± 0.2	0.3	35.1%	No data	2007
02–12	–5.6	–6.7	–10.1	5–6 May 2009	+3.8 ± 0.2	0.1	10.9%	~20–30%	2007
05–36	–7.8	–8.7	–11.1	5–6 May 2009	+3.8 ± 0.2	0.1	5.4%	No data	2007
b09–18	–6.4	–7.4	–15.7	23–24 September 2003	+3.8 ± 0.2	0.2	30.1%	~0–20%	2004
d11–12	–5.5	–6.5	–9.7	6–7 October 2009	+3.8 ± 0.2	0.1	9.5%	~10–30%	2007

^a Reservoir temperatures were measured during the baseline sampling survey and published for the individual wells in Mayer et al. (2013).

^b A reservoir pressure of 170 bar is used for all examples (Hutcheon et al., 2016). Parameters A, B and C are calculated using the published reservoir temperatures and salt contents for

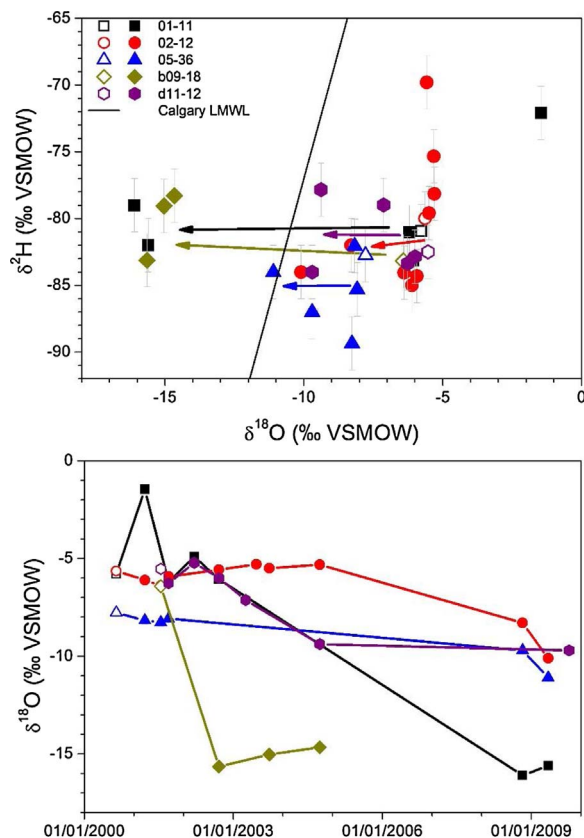


Fig. 4. Oxygen versus hydrogen isotope compositions of reservoir water samples recovered from 5 wells (01–11 in black, 02–12 in red, 05–36 in blue, b09–18 in mustard green, d11–12 in purple) during the IEA GHG Weyburn-Midale CO₂ Monitoring and Storage project (top). The arrows indicate the oxygen isotope shift from baseline conditions over time. The black line indicates the LMWL for Calgary, Canada (Peng et al., 2004). (Bottom) Oxygen isotope data from the same 5 wells plotted over time. Open symbols in both plots are baseline waters, with filled symbols indicating reservoir water samples from the monitoring period. Error bars indicate the maximum analytical error for water $\delta^{18}\text{O}$ ($\pm 0.2\text{‰}$) and $\delta^2\text{H}$ values ($\pm 2.0\text{‰}$); measurement errors for $\delta^{18}\text{O}$ are smaller than or equal to the symbol size. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

from the beginning of CO₂ injection, the injection pattern was dominated by WAG operation (Hirsche et al., 2004). As observed during the Pembina Pilot (Johnson et al., 2011), this may complicate the interpretation of the oxygen isotope shift in the reservoir water since new sources of water with different oxygen isotope ratios and CO₂ saturations are injected that have the potential to disturb the evolving patterns caused by CO₂ injection only. Further, injected CO₂ was

increasingly supplemented by recycled CO₂ obtained from producing wells after CO₂ breakthrough, potentially resulting in variable injected $\delta^{18}\text{O}_{\text{CO}_2}$ values. Consequently, it remains uncertain if the oxygen isotope data from the IEA GHG Weyburn-Midale EOR project can be used to quantify CO₂ pore-space saturation.

3.6. Summary of field project observations

Oxygen isotope data from reservoir water produced during five field projects from around the world provide evidence for isotopic shifts in waters due to oxygen isotope equilibrium exchange with the injected free-phase CO₂ in the reservoir. However, oxygen isotope ratios have only been used to quantify CO₂ pore-space saturation during three of these five field experiments (Frio, Pembina, and Otway 2Bext). Only one single-well field test (Otway 2Bext) has applied oxygen isotopes as a monitoring tool to quantify CO₂ pore-space saturation. The published CO₂ pore-space saturation estimates from the Frio, Pembina and Otway 2Bext projects, as well as the measures from the Ketzin pilot study calculated here, are similar to independent measures of CO₂ pore-space saturation from the respective field tests, further indicating the viability of using oxygen isotope ratios and the Johnson et al. (2011) approach to quantify CO₂ pore-space saturation in cases where the $\delta^{18}\text{O}_{\text{CO}_2}$ values of the injected CO₂ is constant and sufficiently distinct from that of the reservoir water plus $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$. The Pembina and Weyburn-Midale EOR projects suggest that the use of this inherent tracer is problematic when aiming to measure CO₂ pore-space saturation in a WAG regime due to the injection of new sources of water with different CO₂ saturations and oxygen isotope ratios. These new sources of water have the potential to disturb the evolving patterns caused by CO₂ injection only. Other than this potential limitation, the studies revealed important issues that can arise during the use of oxygen isotopes to reconstruct reservoir-scale CO₂ pore-space saturation and that have to be considered when applying this tool, as outlined in the next section.

3.7. Lessons learned about the use of oxygen isotope ratios to quantify CO₂ pore-space saturation during field experiments

The oxygen isotope approach of Johnson et al. (2011) has been applied at different CO₂ storage sites, proving its validity, but also highlighting a number of issues affecting its effectiveness. The key issues for using this technique are:

- 1) The approach provides an averaged saturation over the studied vertical interval,
- 2) The $\delta^{18}\text{O}_{\text{CO}_2}$ value of the injected CO₂ has to be isotopically distinct compared to the $\delta^{18}\text{O}$ value of the reservoir water plus $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$,
- 3) The oxygen isotope composition of the injected CO₂ and reservoir water should be known, and the $\delta^{18}\text{O}_{\text{CO}_2}$ value of the injected CO₂

should be constant throughout the experiment,

- 4) Problems arising from the choice of reservoir water sampling technique and sampling frequency,
- 5) Differences in field projects with CO₂ injection only and WAG operation,
- 6) Complications in the interpretation of oxygen isotope ratios from reservoir water in a single-well test versus an inter-well scenario.

The Johnson et al. (2011) approach provides an averaged saturation over the studied vertical interval, and hence does not take into account potential small-scale vertical variability in the flows of the CO₂ and water (e.g., Kampman et al., 2014). The vertical resolution of the reconstructed saturation will depend on the type of sampling, either sampling at the wellhead, providing an average from the perforated interval, or using a U-tube or other downhole sampling ports, which yield more depth-constrained results.

For an oxygen isotope ratio shift in the reservoir water as a result of CO₂-water oxygen isotope equilibrium exchange in the subsurface to be significantly larger than the analytical uncertainty of $\delta^{18}\text{O}$ measurements, the $\delta^{18}\text{O}_{\text{CO}_2}$ value of the injected CO₂ has to be isotopically distinct compared to the baseline $\delta^{18}\text{O}$ value of reservoir water plus $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$. This is essential for the application of this technique since a small distinction similar to the analytical $\delta^{18}\text{O}$ error results in large uncertainties in estimated X_{CO_2} and S_{CO_2} values based on Eqs. (3) and (4). The Frio and Pembina projects revealed relatively large oxygen isotope shifts in the reservoir water (11.9‰ for Frio and 1.1–3.9‰ for Pembina) as a result of a large difference between the oxygen isotope ratios of the injected CO₂ and the reservoir water plus $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$. The Weyburn-Midale (2.4–9.3‰ change in $\delta^{18}\text{O}$ values of the reservoir water) and Ketzin projects (1.9‰ change) also displayed a clear oxygen isotope shift in the reservoir water, however other issues, which are discussed below, resulted in elevated uncertainties in estimated X_{CO_2} and S_{CO_2} values based on Johnson et al. (2011) from these projects. The Otway 2Bext project was characterised by a small distinction of the oxygen isotope ratios of water and CO₂, resulting in a very small oxygen isotope shift in the reservoir water ($0.3 \pm 0.2\text{‰}$). Consequently, the small oxygen isotope distinction resulted in large uncertainties for the X_{CO_2} and S_{CO_2} estimates from Otway 2Bext.

For the Johnson et al. (2011) method to provide reliable CO₂ pore-space saturation estimates, it is necessary that the baseline $\delta^{18}\text{O}$ value of the reservoir water and the $\delta^{18}\text{O}_{\text{CO}_2}$ value of the injected CO₂ are accurately known and remain constant throughout the experiment. All five field projects described above conducted robust monitoring of the baseline $\delta^{18}\text{O}$ values in the reservoir water prior to CO₂ injection. The Ketzin, Pembina and Weyburn-Midale projects, with water samples collected from different monitoring wells, showed different temporal $\delta^{18}\text{O}$ shift patterns in the reservoir water obtained from the various wells.

While the Pembina and Weyburn-Midale projects provided evidence for essentially constant $\delta^{18}\text{O}_{\text{CO}_2}$ values of the injected CO₂ throughout the injection period, the large variation in $\delta^{18}\text{O}_{\text{CO}_2}$ values of CO₂ injected from a single source during the Ketzin project (varied between -29.3 and -8.7‰ ; Myrtilinen et al., 2010; Nowak et al., 2014) results in large errors for the assumed injected $\delta^{18}\text{O}_{\text{CO}_2}$ value used in Eq. (3) and in estimated X_{CO_2} and S_{CO_2} values. During the Frio experiment, with a single injection and observation well, the injected CO₂ was sourced from a refinery and fertiliser plant, but only an average $\delta^{18}\text{O}_{\text{CO}_2}$ value of $+9\text{‰}$ was reported (Kharaka et al., 2006). No further information is available about the $\delta^{18}\text{O}_{\text{CO}_2}$ values of CO₂ produced by each of the two sources or their mixing proportions. This missing information may introduce large uncertainties in the oxygen isotope composition of the injected CO₂ and its changes throughout the injection period. A solution to this problem is regular monitoring of the injected $\delta^{18}\text{O}_{\text{CO}_2}$ value throughout the injection period, combined with more complex modelling of the CO₂ plume movement in the subsurface. CO₂ from two different sources was injected during Otway 2Bext, with differences in

their oxygen isotope ratios ($+26.1 \pm 0.1\text{‰}$ versus $+29.3 \pm 0.2\text{‰}$). Since no information about mixing of the two CO₂ sources in the reservoir was available, Sermo et al. (2016) assumed perfect mixing and calculated a weighted average based on the injected amounts of the two sources. Considering the small oxygen isotope distinction between the injected CO₂ and reservoir water plus $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$ during this field test and the resulting small shifts in reservoir water $\delta^{18}\text{O}$ values due to CO₂-water oxygen isotope equilibrium exchange, the uncertainty in the $\delta^{18}\text{O}_{\text{CO}_2}$ value of the injected CO₂ results in a significant uncertainty in the estimated CO₂ pore-space saturation.

The reservoir water sampling technique and frequency is another factor that can significantly influence the reliability of CO₂ pore-space saturation estimates. Most CO₂ injection projects were conducted over multiple months or years, with a low frequency of the sampling of reservoir waters. A low-resolution sampling approach potentially results in the inability to observe small-scale temporal and spatial variability because the Johnson et al. (2011) approach averages CO₂ pore-space saturation for the reservoir volume described by each sample. Otway 2Bext was the only field project that collected daily reservoir water samples from the start of CO₂ injection and fluid/gas production, identifying some early breakthrough effects. However, the immediate fluid sampling during Otway 2Bext may have resulted in the collection of water samples that had not established full oxygen isotope equilibrium with the free-phase CO₂ in the subsurface, as it can take up to one week to establish a full equilibrium (Becker et al., 2015; Johnson and Mayer, 2011).

Both the Frio experiment and Otway 2Bext provided evidence that the reservoir water sampling technique can have an important influence on the reliability of the measured water oxygen isotope ratios. Shortly after the initiation of CO₂ injection during the Frio experiment on 4th October 2004, an oxygen isotope ratio difference of $\sim 41\text{--}42\text{‰}$ was established between the sampled CO₂ and reservoir water (Kharaka et al., 2006), which remained constant throughout the monitoring programme (Fig. 5). The reservoir temperature of 60°C in the Frio Formation would result in an oxygen isotope enrichment factor of 33.9‰ following Eq. (2), while an oxygen isotope distinction of $41\text{--}42\text{‰}$ indicates temperatures of $16\text{--}21^\circ\text{C}$. A similar observation has been made during Otway 2Bext when CO₂ samples showed oxygen isotope ratios that were different to those of the water collected from the same U-tube sample by a factor that suggests an equilibration temperature of $\sim 20^\circ\text{C}$. Since samples during the Frio experiment were collected with the same U-tube sampling system used during Otway 2Bext, we suggest that collection of the gas samples at surface may

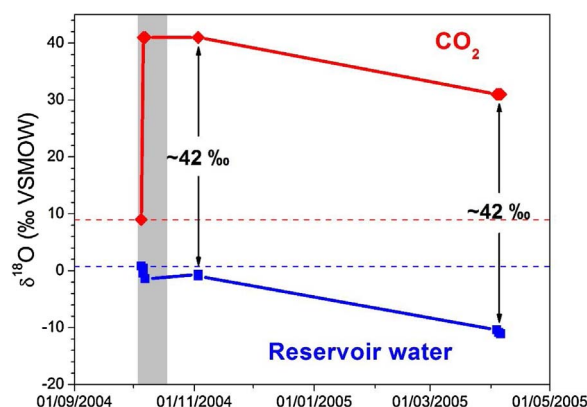


Fig. 5. Change in the $\delta^{18}\text{O}$ value of the reservoir water (blue) and injected CO₂ (red) collected with a U-tube system in the observation well during the Frio-1 experiment (Kharaka et al., 2006), following the period of CO₂ injection at 4–14th October 2014 (grey bar). The blue and red dashed lines indicate the baseline $\delta^{18}\text{O}$ values of reservoir water and injected CO₂, respectively. Shortly after the start of CO₂ injection, reservoir water and CO₂ changed their oxygen isotope composition, and a constant $\delta^{18}\text{O}$ difference of $41\text{--}42\text{‰}$ between the water and CO₂ established. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cause an isotopic equilibrium reaction at surface temperature, which results in a change in the oxygen isotope signature of the CO₂ gas. The water may also be affected by surface degassing, but the degassing will result in a dominance of water in the system and a very small gas volume, and hence a negligible effect on the oxygen isotope composition of the water. However, this may complicate any approach to quantify CO₂ pore-space saturation using the oxygen isotope compositions of both CO₂ and reservoir water, such as applied by Kharaka et al. (2006). Another potential sampling issue at surface was reported by Serno et al. (2016) who found that there were significant differences in the oxygen isotope composition of waters collected at downhole pressure using the U-tube system during Otway 2Bext, which were completely degassed at surface, and those collected from the production line at surface at atmospheric pressure. This observation has been explained to be the result of incomplete degassing of the water sample collected from the production line, which allows continuous oxygen isotope equilibrium exchange between CO₂ and water in the sampling vessel during storage. Therefore, complete degassing of the collected water samples needs to be assured, either through the use of a downhole sampling device or via collection from a surface production line, followed by complete degassing of the sampled reservoir water.

Two of the five field projects that used oxygen isotope ratios as a monitoring tool were fully (Weyburn-Midale) or partly (Pembina) operated in WAG mode, meaning that water and gas were alternately injected, different to CO₂ injection only. WAG operation may complicate the interpretation of observed oxygen isotope shifts in the reservoir water since new sources of water with different oxygen isotope ratios may be injected that have the potential to disturb the evolving patterns caused by CO₂ injection only. Further, injected CO₂ is normally increasingly supplemented by recycled CO₂ obtained from producing wells after CO₂ breakthrough during WAG operations, potentially resulting in variable injected $\delta^{18}\text{O}_{\text{CO}_2}$ values. Immediately following the start of WAG operation during the Pembina Pilot, after a prolonged period of CO₂ injection only, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the reservoir water showed variable responses for the different observation wells, with increasing, constant or decreasing isotopic values as opposed to values prior to the switch to the WAG regime (Johnson et al., 2011). The observations from the Pembina Pilot seem to indicate that the interpretation of oxygen isotope data in terms of CO₂ pore-space saturation during field projects with WAG operation may be problematic. The oxygen isotope data from the single-well Otway 2Bext project showed a very similar problem. Isotopic differences between the two water masses that were injected from two different water storage tanks at surface during the drive to residual saturation and that were produced during Phase 2.4 were identified. Fortunately, Serno et al. (2016) were able to use data of methanol injected into the reservoir water and a simple two-endmember mixing model to calculate the fractions of each of the water masses for each reservoir water sample collected during the production phase. This potential issue is specific to a single-well CO₂ injection project where CO₂ and water are co-injected to drive a formation to residual saturation, and can be resolved by frequent reservoir water monitoring.

There are other issues that can be observed during a single-well experiment, as opposed to a field project with an inter-well configuration. During Otway 2Bext, Serno et al. (2016) found higher S_{CO_2} values further away from the injection well, where the waters thus had a longer reservoir residence time. Although the shifts in the reservoir water $\delta^{18}\text{O}$ values compared to baseline conditions for the different days of production during Phase 2.4 remained constant ($0.26 \pm 0.17\text{‰}$ for day 1, $0.31 \pm 0.15\text{‰}$ for day 2 and $0.29 \pm 0.17\text{‰}$ for day 3), the reservoir conditions varied from day to day, with increasing reservoir temperatures and resulting decreasing $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$ values (from 36.8‰ on day 1–36.0‰ on day 3) and changing parameters A and B, leading to increasing $X_{\text{CO}_2}^0$ and S_{CO_2} estimates based on Eqs. (3) and (4). Considering the changes in reservoir temperature over time, the trend in the oxygen isotope shift for the different days of

water production during Phase 2.4 may be explained by a higher residual saturation further away from the well, but could also be the result of oxygen isotope exchange with mobile CO₂ from ahead of the region driven to residual, or continuous oxygen isotope exchange between reservoir water and residual CO₂ during its back-production. This clearly complicates the interpretation of the change in reservoir water $\delta^{18}\text{O}$ values in terms of CO₂ pore-space or residual saturation during a single-well experiment, but is not crucial for field tests with an inter-well scenario such as the Pembina, Frio, Ketzin and Weyburn-Midale projects.

The oxygen isotope shift in the reservoir water away from baseline values during Otway 2Bext may be simply due to the variable CO₂ volumes the waters were in contact with in the reservoir, with water samples characterised by a longer residence time in the supercritical CO₂-water system from the beginning to end of the production phase. During the back-production, the water may have continued exchanging oxygen with residual CO₂ with variable isotopic signatures in the different regions of the reservoir, resulting in a further perturbation of $\delta^{18}\text{O}_{\text{H}_2\text{O}}^f$. It is difficult to resolve the potential contribution of this mechanism with confidence, mainly due to two factors: 1) The residual CO₂ in the different regions of the reservoir may have already been in contact with other waters and had variable oxygen isotope values compared to the initially injected $\delta^{18}\text{O}_{\text{CO}_2}$, and 2) it is uncertain if there was enough time for continuous oxygen isotope equilibrium exchange of the reservoir water with the residually trapped CO₂ on its way to the well during back-production. This observation could be crucial if considering using oxygen isotopes to quantify CO₂ pore-space or residual saturation in a field experiment using a single-well configuration. We recommend its influence should be studied further in future laboratory experiments with more isotopically distinct CO₂ and water samples and modelling studies.

4. Applicability of the oxygen isotope method to future CCS projects

Whilst pilot projects tend to use natural CO₂ due to abundance and cost, future integrated CCS projects, by their definition, will use anthropogenic captured CO₂. For the oxygen isotope method to accurately quantify CO₂ pore-space saturation, the $\delta^{18}\text{O}$ values of the injected CO₂ and reservoir water have to be isotopically distinct by a value different to $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$. Therefore, to assess whether the oxygen isotope method will be a useful monitoring tool for real-world, commercial CCS, we review the oxygen isotope ratios of captured CO₂ and compare them to the likely range of $\delta^{18}\text{O}$ values of baseline formation waters in storage reservoirs.

4.1. The oxygen isotope ratios of captured CO₂

Industrial processes likely to contribute to CO₂ for geological storage include electricity generation via fuel combustion, gasification processes (e.g. syngas, synfuel and fertiliser production), bioethanol fermentation, steel and cement manufacture, and CO₂ separation processes, applied both to natural gas processing and capture of CO₂. Relevant details of these processes are described by Flude et al. (2016). Sources of oxygen that will contribute to the oxygen isotope ratio of captured CO₂ include: atmospheric oxygen (+23‰; Clark and Fritz, 1997; Kroopnick and Craig, 1972), cryogenically separated oxygen (assumed to be +23‰ but may be higher due to concentration of heavier isotopes in the dense phase during air separation), biomass, limestone (+20 to +30‰; Keith and Weber, 1964), iron ore (+2 to +13‰; Faure, 1986; Nyström et al., 2008), and water and steam. Meteoric waters, excluding regions of extreme climate such as Antarctica, range in $\delta^{18}\text{O}$ values from ~ -20 to +10‰ (Clark and Fritz, 1997). Steam is depleted in ^{18}O relative to the residual water, by $\sim 5\text{‰}$ at 100 °C, and so steam derived from meteoric water will have $\delta^{18}\text{O}$ values between -25 and +10‰, depending on the efficiency of

Table 3
Expected oxygen isotope compositions of CO₂ generated by a variety of industrial and energy generating technologies, relative to their source components (feedstock, combustion, atmosphere, etc.) and with likely oxygen isotope fractionations where relevant, as well as observed oxygen isotope compositions in captured CO₂. Subsequent amine capture and physical absorption are not included.

Process	Oxygen sources and $\delta^{18}\text{O}$ (in ‰ VSMOW)	Modifications to source $\delta^{18}\text{O}$	Hypothetical $\delta^{18}\text{O}_{\text{CO}_2}$ (‰ VSMOW)	Reported $\delta^{18}\text{O}$ of CO ₂ (‰ VSMOW)	
Natural gas processing	CO ₂ in equilibrium with groundwater: +10 to +45, depending on temperature and water $\delta^{18}\text{O}$	Possible small (unknown) fractionation during purification	+5 to +50	+28.6 ± 0.2	Johnson et al. (2011)
Natural combustion	Atmospheric oxygen: ~ +23	Unlikely, but up to -21‰ for biomass due to diffusive fractionation	+2 to +23	+24 to +29	Flude et al. (2017)
Oxyfuel	Cryogenic (atmospheric?) oxygen: ≥ +23	Up to -21‰	+2 to +23	+19 ^b +24 ^b +18 ^b	Nedraussem captured CO ₂ Ferrybridge captured CO ₂ Boundary Dam captured CO ₂
Gasification/Syngas	Steam: -25 to +10 Cryogenic/atmospheric oxygen: ≥ +23	Likely small due to high temperatures involved	-25 to +17	+26.1 ± 0.1 ^c +27.3 ± 0.2 ^c -30 ^a	Callide A Oxyfuel Project plant, Linde AG oil refinery
Fermentation	Meteoric water: -20 to +10 Biomass slightly enriched relative to meteoric water	$\delta^{18}\text{O}_{\text{CO}_2} - \text{H}_2\text{O} = +39$ to +42‰ at typical fermentation temperatures	+19 to +52CO ₂	+14	Scotford Upgrader
Cement	Atmospheric oxygen: ~ +23 Limestone: +20 to +30	Unknown	+21.5 to +26.5	+3.8 ± 0.2	Dakota coal gasification plant
Steel industry: ISP	Atmospheric oxygen: ~ +23	Unlikely, but up to -21	+2 to +23, most likely ~ +23	+9	Bay City refinery and Donaldson fertiliser plant
Steel industry: DRI	CO from syngas: -50 to +23 Iron oxide: +2.3 to +13	Unknown	-24 to +18	+19	Agrium fertiliser plant

^a CO₂ injected at the Ketzin project was a by-product of hydrogen production at the Linde AG oil refinery. The Linde CO₂ was mixed with natural CO₂ prior to injection and published $\delta^{18}\text{O}$ values (-29.3 to -8.7‰; Myrtilinen et al., 2010; Nowak et al., 2014) represent the mixed CO₂. We estimate the $\delta^{18}\text{O}$ value of the refinery component to be -30‰, by correlating published $\delta^{18}\text{O}_{\text{CO}_2}$ with $\delta^{13}\text{C}_{\text{CO}_2}$ and extrapolating to the refinery $\delta^{13}\text{C}$ endmember (-30‰ PDB; Nowak et al., 2014).

^b Combustion-derived CO₂ was purified using amine capture.

^c Combustion-derived CO₂ was purified cryogenically.

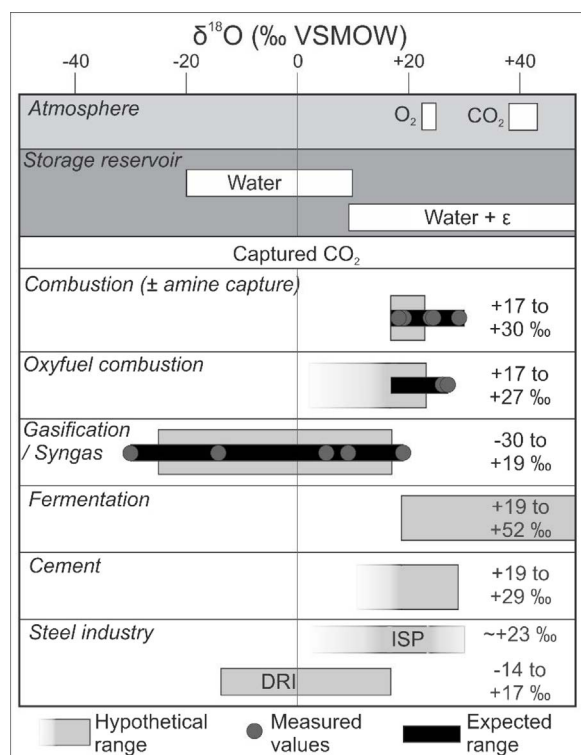


Fig. 6. Range of oxygen isotope compositions in CO₂ produced from the different capture technologies (as shown in Table 3) and from natural sources of CO₂ and oxygen. $\delta^{18}\text{O}$ of atmospheric CO₂ ranges between +38 and +43‰ (Ciais et al., 1997; Clark and Fritz, 1997; Cuntz et al., 2003; Francey and Tans, 1987), while atmospheric oxygen has values between +22 and +24‰ (Clark and Fritz, 1997; Kroopnick and Craig, 1972). Captured CO₂ values are best estimates of the range of $\delta^{18}\text{O}_{\text{CO}_2}$, based on hypothetical considerations and direct measurements. Grey ranges indicate hypothetical values, while the black bars indicate expected ranges. Measured captured CO₂ values are shown as dark grey

converting water to steam. Described data and inferred $\delta^{18}\text{O}$ ranges are presented in Table 3 and Fig. 6.

Combustion-derived CO₂ has been assumed to reflect the $\delta^{18}\text{O}$ value of atmospheric oxygen, but recent work suggests that diffusion-controlled oxygen isotope fractionation may take place during combustion. Isotopic fractionation of up to 21‰ towards lower $\delta^{18}\text{O}$ values was observed for fuels with low ignition temperatures and for burning fuels in an atmosphere with excess oxygen (Schumacher et al., 2011). We would therefore expect combustion-derived CO₂ to have $\delta^{18}\text{O}$ values similar to or lower than that of atmospheric oxygen, with oxyfuel- and biomass-derived CO₂ showing the greatest oxygen isotope fractionation. CO₂ captured from the Callide A Oxyfuel Project, Australia (Uchida et al., 2013), and injected during Otway 2Bext, has a higher than expected $\delta^{18}\text{O}$ value ranging from +26.1 ± 0.1‰ (Serno et al., 2016) to +27.3 ± 0.2‰ (Flude et al., 2017). These higher than atmospheric $\delta^{18}\text{O}$ values were interpreted by Flude et al. (2017) as heavy isotope enrichment during cryogenic purification of both oxygen and captured CO₂, and imply that oxygen isotope fractionation during combustion may not be significant. Flue gas CO₂ derived from air combustion of biomass and natural gas at the Pilot scale Advanced Capture Technologies (PACT) facility (UK) gave $\delta^{18}\text{O}$ values of +24.0 and +29.0‰, respectively (Flude et al., 2017). These oxygen isotope ratios are similar to or higher than those of atmospheric oxygen, suggesting that the expected diffusion controlled ¹⁶O enrichment has not taken place. Captured CO₂ from coal and lignite combustion at the Boundary Dam (Canada), Niederaussem (Germany) and Ferrybridge (UK) combustion power plants have $\delta^{18}\text{O}$ values between +17.8 and +24.1‰ (Flude et al., 2017). These samples were produced by amine capture, which may cause additional oxygen isotope fractionation of

the CO₂. The relative influences of isotope fractionation due to combustion and amine capture remain unknown. However, Flude et al. (2017) concluded that the oxygen isotope composition of water involved during amine capture exerts little influence on the resulting $\delta^{18}\text{O}_{\text{CO}_2}$ value. This conclusion is corroborated by oxygen isotope data from CO₂ injected during the Pembina project. This CO₂ was captured from waste gas streams separated from (presumably Albertan) natural gas at different Ferus Gas Industries facilities, and had a $\delta^{18}\text{O}_{\text{CO}_2}$ value of +28.6 ± 0.2‰ (Johnson et al., 2011) (Table 3). No oxygen isotope data are available for the pre-captured CO₂ co-existing with the natural gas. However, formation waters from oil and gas fields in Alberta have $\delta^{18}\text{O}$ values between -15 and +1.7‰ (Hitchon and Friedman, 1969), and calculating the $\delta^{18}\text{O}_{\text{CO}_2}$ value co-existing with these formation waters gives values between +20 and +35‰ (average of ~ +29‰) (calculation based on temperature and discounting salinity effects). The Pembina CO₂ separated from natural gas thus has an oxygen isotope composition consistent with expected equilibrium conditions in the source reservoirs, and may suggest that oxygen isotope fractionation during amine capture is minimal.

During gasification processes the main source of oxygen is steam, but with up to 50% derived from purified oxygen (Metz et al., 2005). Resulting CO₂ is thus expected to have $\delta^{18}\text{O}$ values between -25 and +17‰. Gasification-derived CO₂ from a range of refineries and chemical plants has $\delta^{18}\text{O}$ values between -30 and +19‰ (see Table 3). For the most part these data are consistent with the expected range of $\delta^{18}\text{O}$ values and small deviations from expected oxygen isotope ratios may be due to changes in the water $\delta^{18}\text{O}$ value during water purification.

Bioethanol is produced from the feedstock by fermentation of the sugars and starches in the biomass, generating a pure stream of CO₂ (Rossmann et al., 1991). While plant transpiration enriches ¹⁸O in plants (and thus their sugars) relative to meteoric water (Monsallier-Bitea et al., 2006), the oxygen contribution from biomass will be minor compared to the volume of added (presumably meteoric) water, which is expected to control $\delta^{18}\text{O}_{\text{CO}_2}$ via $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$. Assuming typical fermentation temperatures of 17–33 °C (Jones and Ingledew, 1994), $\epsilon_{\text{CO}_2-\text{H}_2\text{O}}$ will be between +38.6 and +41.8‰, producing captured CO₂ from fermentation plants with $\delta^{18}\text{O}_{\text{CO}_2}$ values between +19 and +52‰ (Table 3; Fig. 6).

During cement manufacture, ~50% of the CO₂ is derived from calcination of limestone (Ghoshal and Zeman, 2010; Srivastava et al., 2011), with the remainder due to the energy required to fire the kiln (commonly coal or gas combustion). During decarbonation, ¹⁸O is expected to preferentially partition into the CO₂ phase with a $\epsilon_{\text{CO}_2-\text{CO}_3}$ of between +1 and +5‰ (Jolis et al., 2015; Sharp et al., 1996; Shieh and Taylor, 1969). Calcination-derived CO₂ will thus have $\delta^{18}\text{O}_{\text{CO}_2}$ values of +21 to +35‰. Assuming a 50:50 mixture of calcination and combustion-derived CO₂, CO₂ emitted from cement factories are expected to have $\delta^{18}\text{O}_{\text{CO}_2}$ values between +19 and +29‰ (Table 3; Fig. 6), assuming some degree of diffusive oxygen isotope fractionation during combustion.

During steel manufacture, CO₂ is generated from fuel combustion to heat the furnace and from reduction of iron ore (Fe₂O₃, Fe₃O₄) to produce steel via use of reducing agents. Integrated steel plants (ISP) use mostly coal as both fuel and reducing agent (Birat, 2010); combustion is likely to dominate the CO₂ budget resulting in $\delta^{18}\text{O}_{\text{CO}_2}$ values of ≤ +23‰. Mini-mill plants use electric furnaces to heat and melt scrap or direct-reduced iron (DRI) (Metz et al., 2005). DRI is produced by reacting iron ore with syngas to form iron, water and CO₂ (Metz et al., 2005). Up to 50% of the oxygen in the resulting CO₂ would be derived from the CO in syngas, ($\delta^{18}\text{O}$ of -30 to +20‰), with the rest of the oxygen derived from ¹⁸O-enriched iron ore oxides giving $\delta^{18}\text{O}_{\text{CO}_2}$ values between -14 and +17‰ (Table 3; Fig. 6).

4.2. Oxygen isotope ratios of storage formation waters

Baseline oxygen isotope values for formation waters are available from the Pembina (−17.1 to −13.5‰; Johnson et al., 2011), Frio (+0.8‰; Kharaka et al., 2006), Otway 2Bext (−6.3 to −5.6‰; Serno et al., 2006), Ketzin (−5.6 to −5.2‰; Myrtingen et al., 2010), Weyburn-Midale (−9.8 to −1.2‰; Johnson et al., 2009; this study), and CLEAN/Altmark, Germany (−3 to +6‰; Kühn and Münch, 2013) CCS projects. Additional data is available for the Guantao (−10 to −8‰; Pang et al., 2012), and Pontian (−12‰; Varsányi et al., 1997) saline aquifers in China and Hungary, respectively. We thus assume an approximate range in $\delta^{18}\text{O}$ values of −20 to +10‰ for potential storage formation waters. Assuming a range in storage formation temperatures of 25–120 °C, $\varepsilon_{\text{CO}_2-\text{H}_2\text{O}}$ will range between +40 and +26‰.

4.3. Sensitivity of the oxygen isotope method to baseline conditions and determining the optimal $\delta^{18}\text{O}$ value of injected CO_2

Successful calculation of CO_2 pore-space saturation via the oxygen isotope method requires that the co-existing water and CO_2 have a separation between initial $\delta^{18}\text{O}$ values that is different to $\varepsilon_{\text{CO}_2-\text{H}_2\text{O}}$. There will thus be some combinations of initial $\delta^{18}\text{O}$ values and reservoir temperatures that this technique cannot be applied to, and a wider range of conditions where precision of the technique will be limited. Here we assess the sensitivity of the technique for two reasons: 1) to facilitate easy identification of the $\delta^{18}\text{O}_{\text{CO}_2}$ values, and thus CO_2 sources, that will be most useful for residual CO_2 saturation field tests; and 2) to assess the likelihood that the oxygen isotope technique can be successfully applied as a monitoring tool to integrated CCS projects, based on the above reviews of $\delta^{18}\text{O}_{\text{CO}_2}$ and reservoir water $\delta^{18}\text{O}$ values.

An initial assessment of whether the technique can be applied to full scale CCS projects can be made by comparing the “water + ε ” field with the anticipated ranges of $\delta^{18}\text{O}$ values of captured CO_2 shown in Fig. 6. This shows a high potential for overlap of $\delta^{18}\text{O}_{\text{H}_2\text{O}} + \varepsilon$ with $\delta^{18}\text{O}_{\text{CO}_2}$ for CO_2 sourced from most industrial and capture processes and so a more detailed, case-by-case assessment will be required.

The precision and accuracy of CO_2 pore-space saturation estimates based on Eqs. (3) and (4) depends on various parameters, including the $\delta^{18}\text{O}$ values of baseline water and CO_2 , reservoir conditions (temperature, pressure, salinity) and the CO_2 volume that is trapped in the subsurface. We use a simple modelling approach to calculate the potential error on hypothetical CO_2 pore-space saturations using Eq. (4) for a number of conditions, varying the $\delta^{18}\text{O}_{\text{CO}_2}$ value of the injected CO_2 , the $\delta^{18}\text{O}$ value of baseline reservoir water, $X_{\text{CO}_2}^0$ and temperature (or $\varepsilon_{\text{CO}_2-\text{H}_2\text{O}}$) (Fig. 7). In all models, we assumed a constant analytical error of $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ measurements, a reservoir pressure of 150 bar and a reservoir fluid TDS of 0.6 g/L.

Fig. 7 plots the percentage error of the calculated value of CO_2 pore-space saturation against the $\delta^{18}\text{O}_{\text{CO}_2}$ value of the injected CO_2 for different $\delta^{18}\text{O}$ values of the initial water, temperature ($\varepsilon_{\text{CO}_2-\text{H}_2\text{O}}$), and $X_{\text{CO}_2}^0$. This allows an assessment of the ranges of $\delta^{18}\text{O}_{\text{CO}_2}$ values for specific reservoir conditions that will allow accurate estimations of S_{CO_2} with errors < 10%. For $\delta^{18}\text{O}_{\text{CO}_2}$ – water $\delta^{18}\text{O}$ – temperature – $X_{\text{CO}_2}^0$ combinations that plot above the 10% error threshold, the oxygen isotope method will not provide a reliable estimate of CO_2 pore-space saturation.

An important point highlighted by this model is that, for the most effective use of the Johnson et al. (2011) approach, reservoir conditions must be well known. This includes the reservoir temperature, pressure and fluid TDS, but also the baseline $\delta^{18}\text{O}$ range of the reservoir water prior to CO_2 injection.

$\delta^{18}\text{O}$ values of injected CO_2 of less than 0‰ are expected to be the most suitable for applying the oxygen isotope method to full scale CCS projects. The relative error in the CO_2 pore-space saturation estimate is primarily controlled by $X_{\text{CO}_2}^0$. In particular for $X_{\text{CO}_2}^0$ values of > 20%,

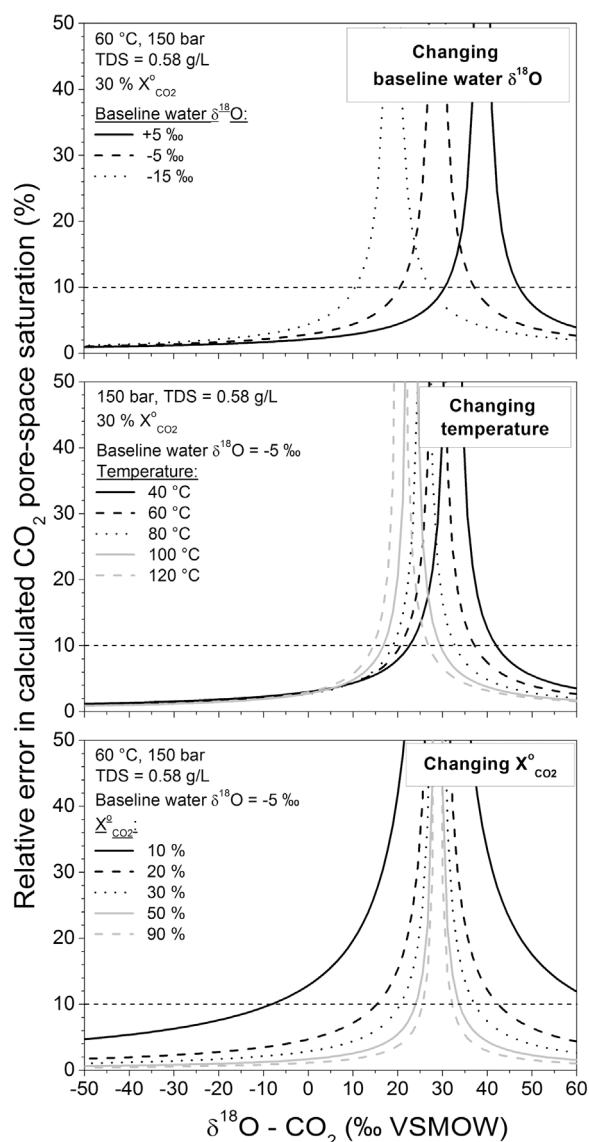


Fig. 7. Relative errors in hypothetical CO_2 pore-space saturations using Eq. (4) for (top) a reservoir with a stable temperature of 60 °C, stable $X_{\text{CO}_2}^0$ of 0.3 and variable baseline reservoir water $\delta^{18}\text{O}$ values (+5, −5 and −15‰), (middle) a reservoir with stable $X_{\text{CO}_2}^0$ of 0.3, a stable baseline water $\delta^{18}\text{O}$ value of −5‰ and variable reservoir temperatures (40, 60, 80, 100 and 120 °C), and (bottom) a reservoir with a stable temperature of 60 °C, a stable baseline water $\delta^{18}\text{O}$ value of −5‰ and variable $X_{\text{CO}_2}^0$ (0.1, 0.2, 0.3, 0.5 and 0.9). In all models, the analytical $\delta^{18}\text{O}$ error, reservoir pressure and fluid TDS are set constant at $\pm 0.2\text{‰}$, 150 bar and 0.6 g/L, respectively. The thermodynamic model of Duan and Sun (2003) was used to derive solubilities and densities of CO_2 in the aqueous NaCl solutions under specified reservoir conditions. Relative errors lower than 10% (indicated by the black dashed line) are acceptable for the estimation of accurate CO_2 pore-space saturations.

the range of $\delta^{18}\text{O}_{\text{CO}_2}$ values that produce relative errors < 10% for S_{CO_2} is rather small. As there are profound differences in reservoir conditions, a comprehensive feasibility study like our simple modelling approach presented in Fig. 7, with additional consideration of the oxygen isotope composition of captured CO_2 (Fig. 6), should be performed in the first stage of each project considering oxygen isotopes as a tool to quantify CO_2 pore-space saturation in a storage reservoir.

5. Conclusions

CO_2 pore-space saturation is a parameter that has been difficult to assess using previous geophysical and geochemical monitoring techniques, but one which is crucial for determining the efficiency of a CO_2

storage site. Our review of studies from CO₂ storage projects around the world illustrates that the oxygen isotope composition of reservoir water changes due to oxygen isotope equilibrium exchange with CO₂ when large amounts of free-phase CO₂ are in contact with the water in the formation. Field experiments at EOR sites in Texas and Alberta show that oxygen isotope shifts in reservoir waters from baseline conditions due to CO₂-water oxygen isotope equilibrium exchange can be used to estimate CO₂ pore-space saturation using a multi-well field configuration (Johnson et al., 2011; Kharaka et al., 2006). Oxygen isotope data from the Otway test facility in Australia were the first from a field project with a single-well configuration that have indicated the potential of using oxygen isotopes to quantify residual trapping levels of CO₂ in a reservoir over a time span of only a few days (Sermo et al., 2016).

Hence, we find that these field, laboratory and theoretical studies provide evidence for the viability of using oxygen isotopes and the Johnson et al. (2011) model to quantify CO₂ pore-space saturation on a reservoir scale during field experiments with either a multi- or single-well configuration. These field tests clearly indicate that it is essential to fully understand the baseline reservoir conditions and oxygen isotope compositions of the reservoir water and injected CO₂ prior to the initiation of injection. This baseline information is necessary to predict the extent of the expected $\delta^{18}\text{O}$ shift in reservoir water. It is also required to estimate the time it takes for reservoir water and CO₂ to achieve full oxygen isotope equilibrium in the formation, which can be up to one week (Becker et al., 2015; Johnson and Mayer, 2011).

We find that a large isotopic distinction of the injected CO₂ and reservoir water (or injected water in case of a single-well CO₂ injection test), considering the temperature-dependent CO₂-water oxygen isotope enrichment factor, is crucial for the development of oxygen isotope shifts in the reservoir water significantly larger than the analytical uncertainty of measured $\delta^{18}\text{O}$ values. The use of a single CO₂ source with a well-defined oxygen isotope signature would avoid uncertainties in the injected $\delta^{18}\text{O}_{\text{CO}_2}$.

CO₂ produced using the various carbon capture technologies can serve as a relatively inexpensive gas source for small or large-scale injection into storage reservoirs (and will ultimately be injected for geological storage). A comprehensive review of the limited data available from captured CO₂, as well as hypothetical considerations of oxygen isotope ranges for the different techniques, indicates that it is currently difficult to specify precise oxygen isotope ranges for the different captured CO₂ sources. Consequently, potential CO₂ sources for storage projects should be analysed prior to injection to assess if oxygen isotopes can be applied as a reliable inherent tracer.

Although oxygen isotopes can provide a simple and inexpensive monitoring technique to quantify small and large-scale CO₂ pore-space or residual CO₂ saturation changes near and further away from a well, it has its known limitations and will not be applicable in all cases. Therefore, a combined geophysical and geochemical monitoring programme would be most effective in determining the fate of the injected CO₂ in a storage reservoir and would provide a commercial operator with greater reassurance of the viability of their proposed storage site in terms of structural and residual CO₂ trapping levels.

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